



Review

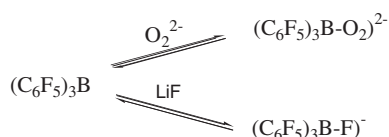
Boron-based anion receptors in lithium-ion and metal-air batteries

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HIGHLIGHTS

- Anion receptors increase lithium ion cell cycle performance and ionic conductivity.
- The boron-based anion receptors also facilitate formation of stable SEI at the electrode surfaces.
- The energetics of the reversible anion binding is modeled by DFT calculations.

GRAPHICAL ABSTRACT



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ABSTRACT

Boron-based anion receptors, widely used as biosensors, are currently being explored as electrolyte-additives in lithium ion batteries and metal-air batteries, towards the goal of realizing high voltage, high energy density batteries. The potential advantage of the boron-based anion receptors as electrolyte-additives is to improve the lithium ion or metal-air battery cell cycle performance, and increase lithium ion transference numbers and ionic conductivity. These anion receptors also have unique characteristics that facilitate in maintaining a stable solid electrolyte interface (SEI) at the electrode surface. In this comprehensive review, we have outlined the synthesis, computational studies, and applications of various classes of boron-based anion receptors in lithium ion and metal-air batteries.

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1. Introduction

Anion receptors that selectively bind to the specific anions, have numerous biological and environmental applications [1,2]. The anion-recognition and binding of these receptors may be due to hydrogen-bonding interactions [3], covalent binding of anions to the substrate [4], or through Lewis acid–base interactions [5,6]. Binding of various anions to the widely used bio- and chemosensors generally results in the change of color or fluorescence

properties of the analytes at millimolar to nanomolar concentrations [6].

Although most of the research in this area is focused on the development of bio- or chemosensors, recent interest in the high voltage, high energy density lithium ion batteries prompted developing novel anion receptors that play a major role in the increased dissociation of lithium salts such as LiF, leading to their enhanced ionic conductivity and increased lithium- and fluoride ion transference numbers. Further, the anion receptors, when used as additives in the electrolyte solvents such as dimethyl carbonate (DMC) or propylene carbonate (PC), dramatically increase the solubility of lithium fluoride (LiF) or lithium oxides (Li₂O and Li₂O₂), and help maintain stable solid electrolyte interface (SEI) at the

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electrode surfaces [7,8]. Tris(pentafluorophenyl)borane (TPFPB), a boron based anion receptor, improves the thermal stability of the SEI formed on a graphite anode [8]. SEI layers are formed normally by the decomposition of the electrolyte materials such as ethylene carbonate (EC) at the electrode surfaces. It was shown that during initial galvanostatic cycling of lithium ion cells, consisting of carbonaceous mesocarbon microbead (MCMB) anode, anion receptors such as TPFPB increase the extent of SEI formation and their thermal stability [9].

Whereas SEI, a protective layer formed on the surfaces of the electrodes during the first charge–discharge cycle, is advantageous in increasing the cell cycle-life, presence of large amounts of insoluble inorganic materials, LiF, Li₂O₂ and Li₂CO₃ in the SEI layers results in increased impedance and capacity loss; anion receptors of appropriate binding affinity can solvate these F[−], HO[−], O₂^{2−} and O₂[−] anions that are present in the protective SEI layers at the anode and cathode surfaces, and facilitate their removal.

Although the mechanisms of the formation of the above lithium salts in SEI is still an active area of research, the following processes are generally believed to be involved: LiF may be formed by the bimolecular nucleophilic substitution reaction (S_N2) of PF₅ a byproduct of PF₆[−] anion decomposition—with alkoxide anion (OR[−]), a highly reactive nucleophilic species. Lithium alkoxide (e.g., LiOMe), in turn, is formed in trace amounts by the electrolytic reduction of the carbonate electrolyte solvents [10,11]. This process has been recently investigated using high level DFT quantum mechanical methods [12].

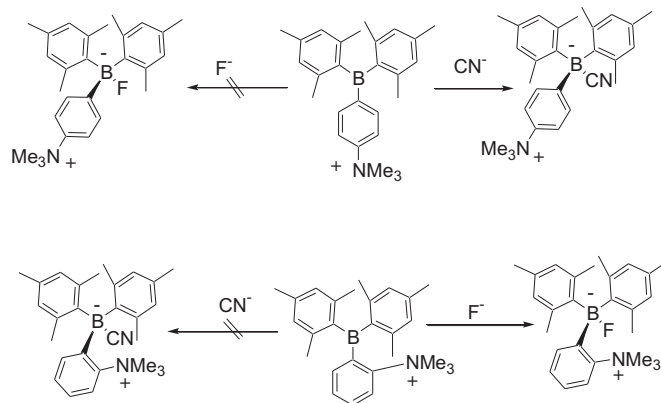
Anion receptors have high importance in the formation of the electrode-protective SEI layers at the anode and cathode surfaces. The efficiency of these anion receptors may be measured by the host-guest stoichiometry and their binding constants [13]. In this comprehensive review, we address the various anion receptors used in the lithium ion batteries, and their synthesis and mode of action. The main focus of the review will be on the boron-based anion receptors as they are readily synthesized and convenient to use as additives in the nonaqueous electrolytes that are commonly used in the lithium ion batteries. Amine-based anion receptors [14–16], which bind anions due to hydrogen bonding interactions, are not discussed here in detail, as they have relatively poor electrolytic stability.

2. Fluoride anion receptors in aqueous solutions

2.1. Fluoride or cyanide specific anion receptors

Boron based anion receptors can be fine-tuned for their selectivity towards fluoride or cyanide anions by adjusting the stereo-electronic effects of the substituents. In particular, it has been elegantly demonstrated that the highly hindered triarylboranes selectively bind to fluoride anion when the electron withdrawing trimethylammonium group is *ortho*- to the boron moiety whereas they are selective to cyanide anion when the cationic substituent is *para*- to the boron moiety [17] (Scheme 1).

Interestingly, this differential selectivity is not found in organic solvents. In aqueous solutions, the fluoride anions are strongly coordinated to water molecules as compared to cyanide anion, and thus relatively more electrophilic boron center (e.g., the *ortho*-trimethylammonium substituted triarylborane) is required for its binding to the receptor. On the other hand, the cyanide anion, being relatively more sterically crowded, would not bind to the latter highly crowded triarylborane. Thus, the electrophilicity of the boranes can be fine-tuned by the appropriate choice of the substituents on the aryl groups so that they can selectively bind to specific anions.



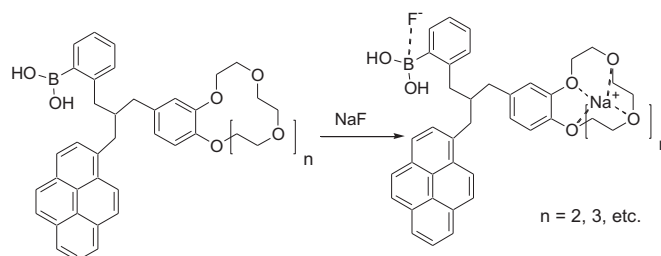
Scheme 1. Triarylboranes as selective anion receptors for fluoride and cyanide anions in aqueous media.

2.2. Ditopic receptors

Ditopic receptors that are selective towards both cations and anions are interesting chimerical compounds as they may help in increased dissociation of the lithium salts, resulting in high anion and cation transference numbers. This concept has not been applied for lithium ion batteries to date. However, ditopic fluorescent sensors having crown ether with appended boronic acid groups have been reported [18] (Scheme 2). The hard boron center would bind to fluoride anions, while the crown ether moiety binds to the cations. In order to be effective receptors for lithium ion batteries, the binding of the cation and anion should be reversible, so that they can be transported from SEI and released into the bulk electrolytes at the appropriate externally applied potential.

3. Effect of anion receptors on ionic conductivity

McBreen and coworkers have prepared a series of trialkyl and triaryl-borates and boranes such as trimethylborate (**1**), tris(tri-fluoromethyl)borate (**2**), tris(heptafluorobutyl)borate (**3**), tris(hexafluoroisopropyl)borate (**4**), tris(perfluoro-*tert*-butyl)borate (**5**), tris(triphenyl)borate (**6**), tris(hexafluorocumyl)borate (**7**), tris(pentafluorophenyl)borate (**8**), and tris(pentafluorophenyl)borane (TPFPB; **9**) (Fig. 1) [19]. These anion receptors were found to complex fluoride anions, and as a consequence, increase the solubility of LiF in nonaqueous electrolyte solvents. In dimethyl ether, for example, the solubility of LiF in the absence of some of these anion receptors is about 10^{−5} M. Upon addition of the boron based anion receptors, the solubility of LiF increased to about 1.2 M, which is about six orders of magnitude higher than that in the absence of the anion receptors. These anion receptors have high electrochemical stability, up to 5.1 V vs Li⁺/Li. The conductivities of their solutions are also significantly higher. When present in equimolar



Scheme 2. Representative example for a ditopic receptor.

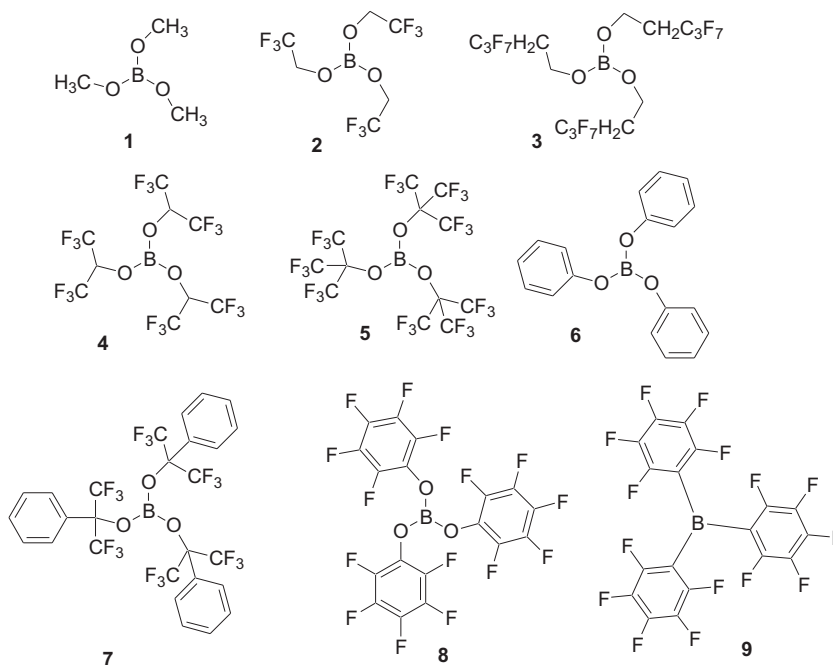


Fig. 1. Structures of various trialkyl/triaryl borates and TPFPB (9).

concentrations, the conductivity of 0.8 M LiF solutions in DME, in the presence of TPFPB was found to be $6 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C. The latter conductivity value is comparable to that of 0.8 M LiPF₆ in DME at 25 °C [19].

As described above, anion receptors have potential advantage of increasing lithium ion battery cell cycle performance and ionic conductivity. Complexation of the electrolyte-derived anions (e.g., fluoride, peroxide, oxide and hydroxide anions) with receptors helps to increase the dissociation of the electrolyte salts, increasing the anion and cation transference numbers. Further, the anion receptors can dissolve and remove the otherwise insoluble inorganic materials such as LiF and Li₂O in the SEI, and thereby increase the ionic conductivity and improve cell performance [20]. The TPFPB, as an electrolyte-additive, increases lithium ion cell performance by removing the LiF from the SEI, as a linear function of its concentration [20]. At relatively higher concentration of the anion receptor, interfacial impedance of the lithium ion batteries increases. It has been postulated that the increased concentration of the anion receptor may accelerate in the formation of PF₅ from PF₆ anions; PF₅ being a strong Lewis acid can catalyze the polymerization of the cyclic carbonate electrolytes and consequent electrolyte poor performance [20].

Difluoro(polyethyleneoxy)boranes ($\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OBF}_2$) have been synthesized by the reaction of the corresponding oligomeric polyethyleneoxy alcohol with BF₃ and used as anion receptors in polymer electrolytes [21]. Ionic conductivities, in the presence of these anion receptors were reported to be 10^{-5} to $10^{-4} \text{ S cm}^{-1}$ at 20 °C to 70 °C, respectively.

3.1. Lithium ion transference numbers

Complexation of the fluoride anion by the Lewis acidic anion receptors results in increased dissociation of the lithium salt based electrolytes (e.g., LiF), and thereby the lithium ion conductivity is expected to increase substantially. In case of the dual ion intercalation batteries [22], the transference numbers of the fluoride anions parallel with those of the lithium ions, which results in

increased power and capacity characteristics of the high energy density lithium ion batteries. In this battery design a new route to reversibly intercalate fluoride-anion receptor complexes in graphite was demonstrated, via a non-aqueous electrochemical process, at discharge plateaus of upwards of 4.8 V; the graphite staging of the intercalant was observed via in-situ synchrotron X-ray diffraction during charging. From these experiments it was inferred that the characteristics of the anion receptor dictate the extent of graphite fluorination.

In order to obtain the maximal specific capacity, it is necessary to identify anion receptors and associated solvents with the following optimal characteristics: (1) Sufficiently wide electrochemical stability window — viz., will not anodically oxidize at the cathode and will not cathodically reduce at the anode during charging; (2) Moderately strong fluoride affinity — if the anion receptor affinity for F[−] is too weak, the LiF will not be drawn into solution at sufficiently high concentration. Conversely, if the fluoride affinity is too strong, the anion receptor will not release the bound F[−] during charging, and will co-intercalate into the graphite cathode; (3) High solubility and diffusivity of the anion receptor complex in the electrolyte.

Critical to cell operation is the release of the anion from the receptor at the cathode/electrolyte interface during charging. To this end, the binding energy of the anion complexing agent can be tailored by manipulating the chemistry of the complexing agents; e.g., electron deficient N or B atoms or electron withdrawing groups can be substituted with weaker binding atoms or groups of atoms.

A first principles calculations-based scheme to identify optimal anion binding energetics, able to both draw sufficient LiF into the solvent as well as releasing the anion at charge potentials near 5 V vs Li/Li⁺ was reported by Blanco, West and coworkers [22] using density functional theory (DFT) quantum mechanics. The energetics of the capture and release of the fluoride anion followed Equation (1), which represents the attractive part of the potential as a Morse curve plus a Gaussian repulsive curve, where D_0 and R_0 are the total binding energy and receptor-F[−] equilibrium distance, E_b and R_b the energy and position of the desolvation release barrier.

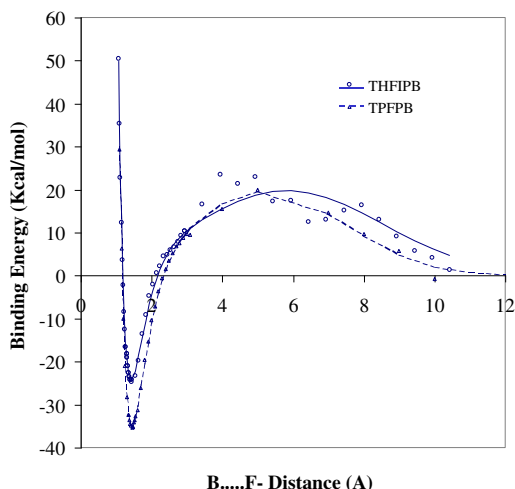


Fig. 2. Binding energetics of two anion receptors at various fluoride ion distances. Note the longer attractive range of tris (hexafluoroisopropyl)borate (THIFPB, beginning at 3.2 Å) when compared to tris(pentafluorophenyl)borane (TFPFB) (2.3 Å). The desolvation barrier at a distance of about 5 Å dominates the anion release kinetics; adapted from Ref. [22].

$$E_{vdw} = D_o \left[e^{-\zeta \left(\frac{R}{R_0} - 1 \right)} - 2e^{-\frac{\zeta}{2} \left(\frac{R}{R_0} - 1 \right)} \right] + E_b e^{-\beta (R - R_b)^2} \quad (1)$$

Two examples of the anion binding energy curves are shown in the Fig. 2 below.

Lithium ion transference numbers in EC/DMC containing LiOTf are increased dramatically in the presence of the anion receptor, TFPFB. Thus upon addition of 0.04 M Kg⁻¹ anion receptor, the lithium ion transference number is increased to 0.94 [23]. The transference numbers are also dependent on the electrolyte systems, and in some cases there is no noticeable effect upon addition of the anion receptors [23].

4. Boron based anion receptors

4.1. Trialkyl(aryl) borates

The relatively inexpensive tri(*n*-propyl)borate and related borates (Fig. 3) have been explored as a potentially valuable electrolyte additive- anion receptor [24]. The performance of the MCMB/LiMnCoO₂ cells with LiPF₆ is improved upon addition of <0.1 weight % of the borate. Large amount of the borate anion receptor resulted in the release of a small amount of unknown gas, and deteriorated the cell performance when cycled at 55 °C.

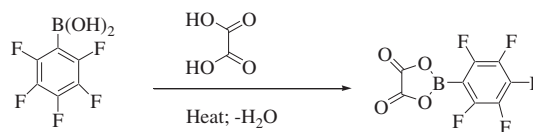
Triphenylborate, as electrolyte additive in lithium ion batteries, using LiFePO₄ cathode and 1:1 EC-DMC, shows formation of a thick SEI, which is impervious to ion flow. Even though it is a useful electrolyte additive at 25 °C, it shows only 7% capacity after 100 cycles at 60 °C. On the other hand, use of 0.1 M trimethylborate results in 53% capacity, and it also suppresses the electrolyte degradation and forms a better SEI as compared to that of triphenylborate [25].

4.2. Bifunctional anion receptors

Pentafluorophenyl(oxalato)borate (PFBO), as an additive to the electrolytes, serves as an efficient anion receptor. It is



Fig. 3. Structures of tri(*n*-propyl)borate, triphenylborate, and trimethylborate.



Scheme 3. Preparation of pentafluorophenyl(oxalate)borate.

electrochemically stable to LiMnO₄ cathodes and MCMB anodes, and is a bifunctional additive such that it serves as an anion receptor for dissolving LiF and other inorganic impurities in SEI including Li₂O and Li₂O₂, while at the same time, it helps in the formation of stable SEI layers at the electrode surface [7]. The synthesis of PFBO is achieved by dehydrative condensation of oxalic acid with pentafluorophenylboronic acid (Scheme 3).

The lithium dioxoloborate (LiBOB) is popularly used as solid electrolyte interface (SEI) forming material in lithium ion batteries [26,27]. Xu and coworkers have introduced a modified version, lithium difluoro(oxalate)borate (LiDFOB) as an improved material for forming SEI [28]. LiDFOB increases electrolyte thermal stability and forms better SEI on graphite anodes and LiFePO₄ cathodes. It also gives better capacity retention to the cells.

The bifunctional PFBO can thus act as a dual function agent, in the formation of stable SEI on the electrode surface and in the removal of the LiF and other inorganic materials from the SEI.

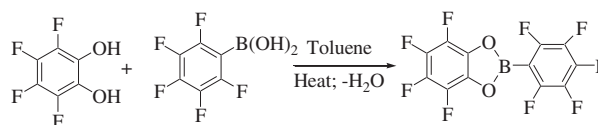
4.3. Anion receptors in gel polymer electrolytes

Poly(ethylene glycol)borate is used as anion receptor material in gel polymer electrolyte systems, by coating the anion receptor onto the microporous polyethylene separators. Increasing the concentration of the anion receptor resulted in the increase of the cationic conductivity in the cell [29].

4.4. Fluorinated 1,3,2-benzodioxaboroles

Recently, a highly fluorinated boronic ester, 2-(pentafluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole (PFPTFBB), synthesized through dehydrative condensation of tetrafluorocatechol and pentafluorophenylboronic acid, was shown to have overcharge protection characteristics (Scheme 4) [30,31]. PFPTFBB has a cathodic stability of 4.43 V vs Li⁺/Li, and thus it serves for overcharge protection and as anion receptor in conventional carbonate based electrolytes. This additive provides overcharge protection for MCMB (Mesocarbon microbeads)/LiNiCoAlO₂ cells with LiPF₆ as supporting electrolyte for over 50 cycles, but it fails to give any overcharge protection for LiBF₄ containing cells. However, at present the synthesis of this compound suffers from the lack of commercially available pure tetrafluorocatechol and the multistep synthesis involved in the preparation of this compound.

Similar boron-based anion receptors having difluorophenyl and bis(trifluoromethyl)phenyl substituents have also been reported by Amine and coworkers (Fig. 4) [32]. The electrochemical performance (capacity retention) using these anion receptors suffered greatly, and it may be due to the relatively lower affinity for fluoride anions, and their tendency to polymerize the carbonate based



Scheme 4. Preparation of B-pentafluorophenyl-1,3,2-benzodioxaborole.

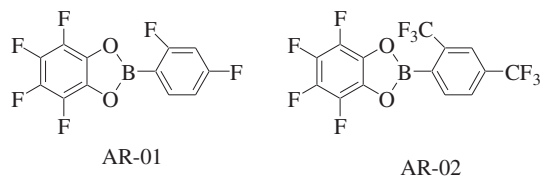


Fig. 4. Structures of 1,3-dioxaboroles, AR-01 and AR-02.

electrolytes. The decomposition or polymerization of the carbonate electrolytes may be initiated by the strongly Lewis acidic PF_5 , which is formed by the transfer of the fluoride anion from hexafluorophosphate anion to the anion receptor. Thus, anion receptors should be kept to as low concentration as possible to avoid the unexpected polymerization of the carbonate electrolytes. These side reactions may be eliminated by the use of non-carbonate based electrolytes, such as ionic liquid based electrolyte solvents. The possible mode of polymerization of ethylene carbonate is shown below (Scheme 5). Ab initio calculations show that the electrochemical performance is correlated with the degree of localization of the LUMO of the anion receptors.

The ab initio calculations show that the fluoride anion affinity of anion receptors decreases with increase in the number of oxygens attached to the boron [33]. Thus, trialkoxyboranes have relatively less fluoride affinity as compared to dialkoxyalkylboranes, which, in turn, have lower affinity to fluoride as compared to trialkylboranes. The fluoride affinity increases with increase in the number of electron withdrawing groups such as F and CF_3 groups, also in accordance with our previous DFT calculations on fluorinated boroxines [13]. These calculations also show that for the anion receptors having the same number of fluorine atoms, the higher the flexibility of the molecule the higher the fluoride anion binding energy [33]. AR-21, for example, has a fluoride anion binding energy of $411.8 \text{ kJ mol}^{-1}$ whereas the less flexible AR-12 has a fluoride binding energy of $384.3 \text{ kJ mol}^{-1}$ (Fig. 5). These solvation energetics may be overestimated due to the small basis set (6–31 + G(d)) used in these calculations.

4.5. Boroxines as anion receptors

We have demonstrated the fluorinated boroxines as fluoride-specific anion receptors in nonaqueous carbonate-based electrolytes [13,34]. The synthesis of boroxines is convenient and amenable to prepare a series of fluorinated and variously substituted boroxines.

The corresponding boronic acids are readily transformed to the cyclic boroxines by dehydrative cyclizations in quantitative yields (Scheme 6). Structures of the boroxines were confirmed by multi-nuclear highfield NMR (^1H , ^{13}C , and ^{11}B NMR) and mass spectrometry (EI and ESI-MS). Our DFT theoretical calculations show that increasing the number of the electron-withdrawing fluorine

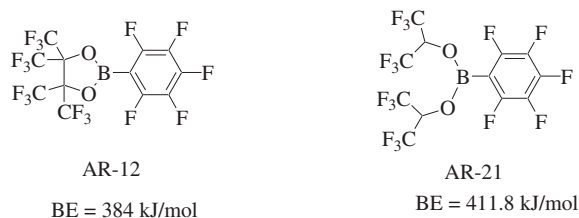


Fig. 5. Structures of B-aryl-1,3,2-dioxaboroles, AR-12 and AR-21, and their fluoride anion binding energies (BE).

groups on the aryl groups increases fluoride anion receptor ability. Fluoride anion binding energies at B3LYP/LACVP** level of calculation for representative fluorinated boroxines are shown below [13,34] (Fig. 6).

Interestingly, the binding energy for the second and third fluoride anion capture is also exothermic. In case of (2,6-difluorophenyl)-bis(pentafluorophenyl)boroxine the second and third fluoride anion binding energies are $49.1 \text{ kcal mol}^{-1}$ and $16.6 \text{ kcal mol}^{-1}$, respectively. The second fluoride anion binds to the more fluorinated bis(pentafluorophenyl) group, and the third fluoride anion attaches to the remaining free 2,6-difluorophenyl group.

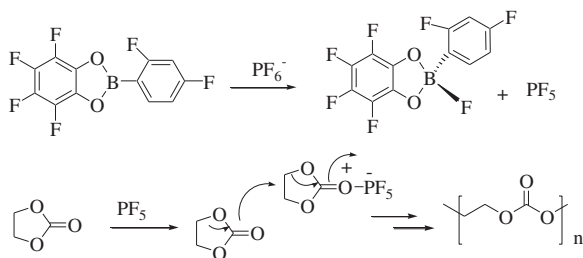
Various fluorinated triarylboroxines, such as tris(2,6-difluorophenyl)borane (DF), tris(2,4,6-trifluorophenyl)borane (TF), and tris(pentafluorophenyl)borane (PF) have been synthesized by dehydrative trimerization and investigated for their relative fluoride anion binding [13,34]. All of these boroxines bind to fluoride in a 1:1 stoichiometry as shown by UV–vis Job's plot and high resolution electrospray ionization mass spectrometry (ESI-HRMS) [8]. The fluoride anion binding to all of these boroxines is reversible, as confirmed by our mass spectrometric and ^{19}F NMR investigations. The fluoride anion migrates intramolecularly with an upper limit of 12 kcal mol^{-1} for 1,2-fluoride shift, as shown by ^{19}F NMR and ^{11}B NMR spectroscopy. Our DFT calculations show that the unsymmetrically bound fluoride anion complex is more stable than the symmetrically bound complex by $12.5 \text{ kcal mol}^{-1}$. The ionic conductivities of 0.2 M LiF in PC in the presence of 0.1 M DF, TF, or PF is significantly increased and this increase in ionic conductivity is comparable to that of the tris(pentafluorophenyl)borane additive at similar concentration [13].

4.6. Trialkoxyboroxines as anion receptors

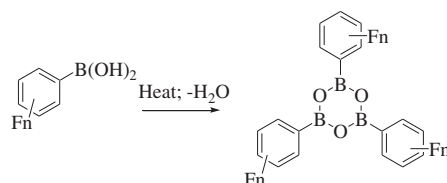
Fujinami and coworkers have explored trialkoxyboroxines (Fig. 7) as the anion receptors [35]. Interestingly, electrolyte oxidation potentials are increased upon addition of these boroxines. Thus, the anodic stability of the carbonate-based electrolyte solution consisting of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) is increased to 5 V vs Li^+/Li for the mixture of tris(4-isopropoxy)boroxine in EC/EMC [35].

5. Borate ester based anion receptors

Recently, a new class of borate esters that can be fine tuned for their anion receptivity have been reported [36] (Scheme 7). The



Scheme 5. Suggested mechanism for the polymerization of EC by the B-aryl-1,3,2-dioxaborole.



Scheme 6. Preparation of triarylboroxines.

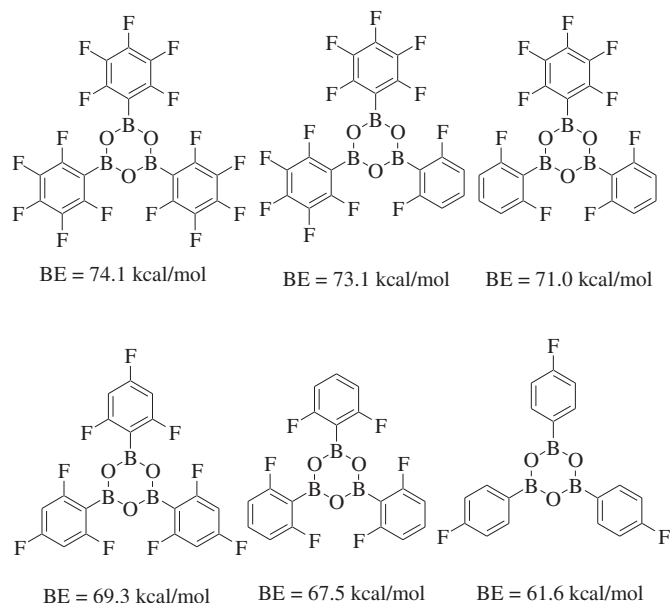
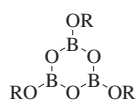


Fig. 6. DFT (B3LYP/LACVP**) deriv - d fluoride binding energies (BE) for various fluorinated boroxines.

borate esters are readily available by transesterification of the corresponding alcohols or hydroxycarboxylic acids with a trialkylborate. Using ^{11}B , ^{19}F , and ESI-HRMS techniques, it was shown that these borate esters form multiple complexes with anions and they are formed reversibly; i.e., the fluoride anion is reversibly complexed to three, two, or one borate molecules. The rapid exchange of the anions allows these borates to act as a catalytic shuttle in the transfer of the lithium oxide, lithium fluoride and other insoluble materials from SEI to the liquid electrolyte media. The conductivities of various salt solutions (e.g., LiF, NaF, KF, Li_2O , and Li_2O_2) were examined in a variety of solvents in the presence of these triolborates and their acid derivatives, and in each of these cases it was observed that there is a marked increase in conductivities of the solutions in the presence of the anion receptors (Fig. 8) [36]. Of all these borates studied, the nitro-triolborate has highest electrochemical stability, 1–5 V vs Li^+/Li [36]. These anion receptors, when optimally modified by electron withdrawing or electron releasing groups are expected to provide cheaper alternatives to the currently used fluorinated anion receptors.

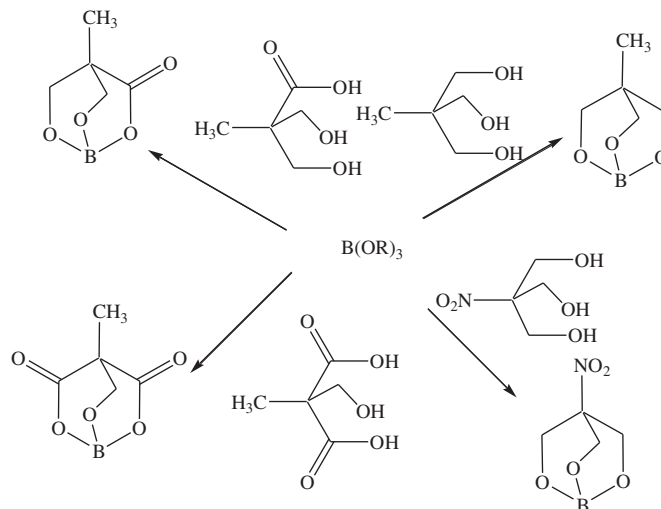
6. Anion receptors for enhanced rechargeability in metal-Air batteries

Reduction of the molecular oxygen at the negative electrode gives superoxide anion (O_2^-), which upon further reduction or disproportionation yields Li_2O_2 and eventually the least soluble, most difficult to oxidize species, Li_2O . LiOH may also be formed due to the reaction of trace amount of water impurities present in the carbonate solvents. A recent surge of interest in developing an organic electrolyte containing rechargeable lithium-air (oxygen) battery stems from the fact that it offers one of the highest theoretical gravimetric energy densities in electrochemical energy



R = e.g., Me, Et, Bu, isopropyl

Fig. 7. Structure of trialkoxyboroxines.



Scheme 7. Preparation of triolborates and acid-alcohol-borates.

storage devices [37–42]. However, this promising high energy density technology currently is at its very early stage of development, with several formidable scientific and technical challenges that must be overcome before it becomes a viable alternative to conventional Li-ion batteries. Much of the recent developments and challenges facing Li-air batteries is summarized in several excellent reviews [43–45]. One of the prerequisites for the development of rechargeable Li-air batteries that have high capacity and high cycle number is the identification of electrolyte materials that are not consumed or decomposed in the air cathode during cell operation.

A second strategy is to bind the reactive anions away from the solvent. The superoxide anion radical ($\text{O}_2^{\bullet-}$) is thought to be responsible for the decomposition of carbonate solvents [46–51]. Important evidence comes from the irreversibility of the $\text{O}_2/\text{O}_2^{\bullet-}$ redox couple in the propylene carbonate (PC) solvent containing

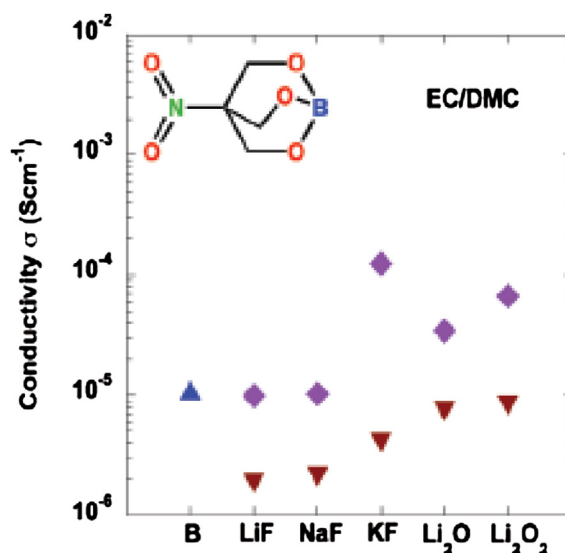


Fig. 8. Conductivities of various salts (LiF, NaF, KF, Li_2O , Li_2O_2) in EC/DMC in the presence (purple) and absence (red) of a triolborate; the conductivities are significantly higher for each of these salt solutions in the presence of the triolborate (adapted from reference [36]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Scheme 8. Reversible and irreversible binding of TPFPB with peroxide anion and superoxide radical anion, respectively, to give the TPFPB-peroxide adduct.

large organic cations [43,52]. However, until recently, there was a lack of clear understanding of the major mechanism of decomposition of carbonate solvents by superoxide radical anion. In a recent communication [12], using density functional theory and coupled-cluster calculations, it has been demonstrated that the nucleophilic attack of $\text{O}_2^{\cdot -}$ at the alkoxy carbon atoms is a common mechanism for the degradation of the carbonate-based electrolyte solvents. Thus, anion receptors have been proposed as the means to increase the capacity and rechargeability of metal-air batteries through solvent protection and the enhanced recovery of electrically insulated oxygen reduction products [53,54].

The TPFPB anion receptor binds to peroxide anion and forms a thermodynamically stable species that could be electrochemically oxidized with improved kinetics than the oxidation of solid Li_2O_2 on a carbon powder microelectrode. The superoxide radical also forms the TPFPB-peroxide anion complex through disproportionation mechanism (Scheme 8) [55]. Due to this complex formation, the solubility of Li_2O_2 in PC/acetonitrile (1:5 v/v) in the presence of 0.5% (0.0391 M) TPFPB is increased by 27 times as compared to that of Li_2O_2 in the absence of the anion receptor [55]. Li_2O_2 saturated PC/acetonitrile solution shows no oxidation current on the carbon powder microelectrode due to the low solubility of the peroxide in this solvent. However, addition of 0.5 wt% of TPFPB to this solution results in substantial oxidation limiting current. Further, the use of a small amount of TPFPB anion receptor attenuates the oxidative reaction of superoxide radical anion with PC, and the PC/acetonitrile solvent may be used in the lithium-oxygen batteries [55]. Other carbonate based electrolyte solvents such as EC/EMC (ethylene carbonate/ethyl methyl carbonate) also similarly can be used in lithium oxygen batteries, using the TPFPB anion receptor [7]. The improved dissociation of Li_2O_2 by TPFPB may reduce the charge potential of the Li_2O_2 cathode during the first charge cycle, so that high discharge capacities may be achieved for the lithium-oxygen batteries. Thus, the first discharge capacities of Li_2O_2 /super P/PVDF electrodes are substantially increased in the presence of the TPFPB (814 mAh g^{-1}), as compared to that without the anion receptor additive (277 mAh g^{-1}) [7]. These interesting observations suggest the possibility of using appropriate boron-based anion receptors as electrolyte additives for the development of high capacity, high rate rechargeable lithium- O_2 batteries.

7. Conclusion and outlook

The use of anion receptors in Li-ion and Metal-Air batteries is a fast-growing area of research. The anion receptor selectivity and energetics can be fine-tuned to meet the required needs of a particular application, i.e., through the appropriate binding and the optimal release energetics. In some instances the anion receptor function is directed towards added solubility of a precipitated product such as lithium peroxide, increasing electrolyte conductivity, while in others the primary function may be that of protection of the surrounding media, such as electrolyte solvent from the strong base afforded by the anion, or the transport of the anion for oxidation at the cathode during recharge. Further, the boron-based anion receptors would have important applications in lithium ion batteries in maintaining the stable SEI layers on the electrode surfaces and as overcharge or over-voltage protectors.

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